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DETERMINATION OF THE SENSITIVITY AND SPECIFICITY OF VAPOR DETECTION SYSTEMS FOR EXPLOSIVES, NARCOTICS, AND RELATED COMPOUNDS

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DETERMINATION OF THE SENSITIVITY AND SPECIFICITY OF VAPOR DETECTION SYSTEMS FOR EXPLOSIVES, NARCOTICS, AND RELATED COMPOUNDS

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During the past decade a number of portable vapor detection systems have been developed in response to military and law enforcement problems. In view of its early R&D involvement in this area, the US Army Land Warfare Laboratory initiated an internal program with the objective of evaluating the capabilities of certain of the most promising of these detection systems. The emphasis of the program has been on those systems capable of detecting explosives, narcotics, and compounds related to the production of these materials. In the course of the evaluation, the following detection systems have been examined: (1) Ion Mobility Spectrometer (a type of plasma chromatograph), Franklin Institute Research Laboratories; (2) Bioluminescent Sensor System, RPC Corporation; (3) Portable Quadrupole Mass Spectrometer, Varian Associates; (4) Model 27 Celignite Detector and Model 58 Explosive Detector, Ion Track Instruments; (5) Explosive Detection Dogs, trained by Southwest Research Institute. All of these systems have the feature of direct sampling of the atmosphere.

The most significant criteria of performance of a detection system are its sensitivity and specificity, since by a correlation of information regarding these characteristics it should be possible to predict the effectiveness of a system in a proposed operational environment. For this reason the USALWL program has been concerned principally with determining these characteristics for a variety of detection systems. The sensitivity of a detection system for the vapor of a given compound has been taken to be the threshold concentration for a detection under ideal conditions. To be meaningful, this threshold concentration must be determined experimentally rather

than theoretically. A two-stage gas dilution system was designed and constructed to serve as a source of appropriate vapors. By its use the detection systems listed above have been calibrated with regard to sensitivity for one or more compounds, and may be directly compared with each other.

The second significant characteristic of a detection system is its specificity, that is, its ability to distinguish a particular vapor from the plethora of vapors which may be present in any given environment. With the exception of trained dogs, each system was allowed to sample numerous vapors with a reasonable probability of being encountered in operational situations. Those vapors were determined which either resulted in false detections or acted as interferences, thereby reducing the effecting sensitivity of each detection system.

The compounds selected for sensitivity studies were ethylene glycol dinitrate (EGDN), trinitrotoluene (TNT), acetic anhydride, and cocaine. EGDN is a substance added to nitroglycerine in the preparation of low freezing dynamites, has a vapor pressure approximately two orders of magnitude higher at room temperature than nitroglycerine, and is known to be the principal vapor above dynamite. The choice of TNT is obvious, but it should be emphasized that the sensitivities were measured for TNT, with virtually all dinitrotoluene (DNT) vapor eliminated. Acetic anhydride is utilized in processing morphine into heroin and is expected to be found either in the area where such processing is done, or as a trace impurity in heroin. Like heroin, acetic anhydride decomposes in the presence of water vapor to form acetic acid. The choice of cocaine is clear, but it had to be heated because of its very low vapor pressure. Although heroin was briefly studied, we suspect it underwent thermal decomposition before being detected. Finally, a measure of the specificity of each of the first four systems has been established from its response to a list of more than fifty selected compounds.

I. MEASUREMENT TECHNIQUE

The threshold concentrations for a response by the detection systems ranged from less than one to more than a hundred parts per billion (PPB), where concentrations are defined in terms of a ratio of moles of sample to be detected to moles of carrier gas. In order to determine sensitivities, a method of accurately generating such concentrations in a purified carrier gas had to be developed. Figure 1 is a diagram of the closed, two-stage dilution system which was developed for this purpose.

The initial stage of the dilution system consists of a DuPont Thermograviometric Analyzer (TGA) used to vaporize specific compounds and a mixing tube. The TGA measures directly the change in weight of a sample material as a function of temperature or time. A metered inert gas flow is directed into the TGA and mixes with evolving sample vapors. The gas mixture emerging from the TGA enters a heated glass line where further mixing occurs. Typical concentrations at this point range from $1:10^3$ to $1:10^5$. Further reduction of concentration is obtained by metering a small portion of this mixture into the heated, second stage of the system. This is accomplished by means of a pressure difference across an orifice connecting the two stages. The second stage also has a carrier gas flowing through it, which in turn mixes with the flow through the orifice and produces the final concentration of the mixture. After a suitable length for uniform mixing, the detection system terminates with several ports, of which one is used as a sample port for the detectors. A portion of the final mixture is also diverted to a mass spectrometer and/or previously calibrated electron capture or flame ionization detectors. These units serve to verify the final concentrations being seen by the detection systems under evaluation.

In the specificity portion of the evaluation, the responses of all but the last detection system were noted when they sampled the vapors of a series of common compounds or compounds of interest. Each detector was allowed to "sniff" for five seconds at the top of a container partially filled with one of the selected compounds. The containers were approximately 5 cc's in volume and generally were less than half full. No attempt was made to estimate the concentrations of vapor sampled by the detectors.

II. RESULTS

A. ION MOBILITY SPECTROMETER

The Ion Mobility Spectrometer (IMS) is a version of the Plasma Chromatograph which was originally built for USAMWL by Franklin GNO and modified by Franklin Institute Research Laboratories. The underlying concept of the instrument is that ions can be distinguished from one another by their mobility in a uniform electric field. The particular version tested was designed for real-world use, operates at atmospheric pressure, and utilizes neither ultra-pure carrier gases, nor heating of the detector.

Figure 2 is a diagram of the interior configuration of the IMS. Samples of air are continuously drawn into the instrument and

swept past a Ni^{63} beta emitter. The beta particles ionize molecules in the air and, in turn, the ions may interact with other molecules. Although the kinetics involved are quite complicated and not completely understood, the net result is a region of ionized species near the shutter grid at the entrance to the drift tube. The drift tube has a cylindrical shape and a radially-independent electric field is imposed along its axis. However, the shutter grid acts as a gate to prevent ions from randomly entering the tube. When the grid is "opened" ions of the proper charge accelerate into and down the drift tube, undergoing multiple collisions with neutral molecules, and eventually being collected and measured as a current by a fast electrometer. The mobility of an ion depends on a number of factors such as its mass, charge, effective ionic size, and so forth. It was claimed that ionic mobility differences would result in a separation of ionic species into disc-shaped envelopes whose time of flight would characterize the species, in analogy with the retention times of gas chromatography.

The IMS operates in a continuous mode, with the shutter grid opening for a fraction of a millisecond every 25.6 milliseconds, and with a detection mode for either positive or negative ions. Data are visually displayed on a scope in the form of a spectrum of current versus time over the 25.6 millisecond period. Those spectra toward the left side of Figure 3 (a)-(d) are typical clean air spectra. It is believed that the "air peak" is due to ions chiefly of the form $(H_2O)_n\ NO^+$ and $(H_2O)_m\ H^+$ in the positive detection mode, $(H_2O)_n\ CO_3^-$ and $(H_2O)_m\ O_2^-$ in the negative detection mode. These ions are termed reactant ions, because they can interact with trace molecules in the air to produce additional ionic species.

The response of the IMS to low concentrations of compounds of interest in air was investigated for both its positive and negative detection modes. For detectable compounds it was found that the time of flight of the predominant species was dependent on the concentration of the parent compound in air, showing an increasing time of flight with increasing concentration. In Figure 3, this is manifested by the shift of the "pure air" peak to the right (to longer times of flight) as the concentration of acetic anhydride in air is increased. While the sequence shown for acetic anhydride occurred in the positive detection mode, a similar response to detectable compounds such as EGDN was noted in the negative mode.

Our tests confirmed that the IMS is quite sensitive to the presence of a number of compounds, in the sense that a shift in the spectrum is discernable at very low concentrations. For instance, a concentration level of 4 PPB for acetic anhydride or of 25 PPB for

EGDN causes a shift which corresponds to an increase of 0.3 milliseconds in the time of flight of the predominant species. However, since the IMS responds to many compounds in the same manner, at very low concentrations there is no possibility of identifying which compound is being detected. One must conclude that the IMS - this real-world version of the plasma chromatograph - has virtually no specificity at low concentration levels and is presently not a useful detector.

B. BIOLUMINESCENT SENSOR SYSTEM

There are in nature certain types of marine microorganisms which have the property of luminescing during their life cycle. Under proper conditions they are not only capable of existing outside their normal water environment, but also continue to luminesce in the atmosphere. It has been found that, when they are exposed to the vapors of chemical compounds, these microorganisms may exhibit a change in the intensity of their luminescence. Attempts have been made to develop strains of the microorganisms which not only have a reasonable specificity for certain vapors, but also a greatly improved sensitivity. The RPC Corporation has developed strains for the detection of quite a wide range of compounds including dynamite (EGDN), TNT, acetic acid and acetic anhydride.

For the RPC Dual Chamber Bioluminescent Sensor System which was tested, microorganisms are grown on a nutrient medium in a cartridge and this is referred to as a sensor. After the microorganisms mature, the sensor is placed in a chamber facing a photocell. When the sensor is exposed to the vapors of some compound, there may result in an increase, decrease, or no change in its luminescent intensity. A sensor which shows an increased or decreased light emission in the presence of a compound one wishes to detect is called a positive or negative sensor, respectively, for that compound. Whenever possible, a pair of sensors - a positive and a negative sensor - are used together for improved specificity, since a single sensor may respond with a false detection to a number of vapors. There are pairs of sensors for both EGDN and acetic acid/anhydride, but only a negative sensor for TNT at the present time.

The Dual Channel Sensor System is the most portable of all the detection systems examined. The system consists of two basic compounds: A handheld probe which contains the sensors, and an electronic control box. It is small, lightweight and has a low power requirement which allows it to operate off a small battery pack. In operation, a single sensor functions efficiently for four to six hours under normal conditions and for two hours or less in a hot-dry

or contaminated environment. Aside from specificity problems described below, the principal disadvantage of the detector is the necessity of beginning sensor preparation from 18 to 30 hours before anticipated use.

The evaluation of the system showed that the unit had a reasonable sensitivity for the compounds of interest. The threshold concentration level in air was found to be approximately 15 PPB for EGDN, 30 PPB for TNT and 24 PPB for acetic anhydride. The above values were obtained for the most sensitive sensor strains developed prior to the tests. Furthermore, these values were determined by analyzing the signal output of the detector on an external chart recorder. The internal alarm system of the detector itself is somewhat insensitive and should be improved.

There are definite specificity problems with the biosensor system. For each type of sensor or sensor pair, there are a number of common compounds such as gasoline whose vapors give false detections. In addition, a detection-like response occurs whenever there is a sudden change in humidity of the air being sampled. False detections constitute a particularly serious difficulty for the single TNT sensor and are an ever present problem for the sensor pairs. It is the opinion of the authors that there is a sufficient degree of specificity for the sensor pairs, so that in a normal environment a well trained and experienced operator can recognize most sources of false detections and can effectively use this detection system.

In summary, the Bioluminescent Sensor System has sufficient sensitivity and specificity to be operationally effective, although the hazard of false detections remains. The system's portability can make it particularly useful in covert operations.

C. MASS SPECTROMETER

A portable, quadrupole mass spectrometer was designed and built by Varian Associates according to USAWL specifications. In order to meet the requirement of portability, the design incorporated such features as a three-stage, Llewellyn membrane separator with variable temperature control, a "portable" vacuum system, and a program control and data processing system based on a small, general purpose computer. Silicone elastometric membranes in the separator act as a concentrator, efficiently transmitting organic materials with normal boiling point between about 0°C and as high as 400°C, while excluding to a large extent the air gases. Thus, vacuum requirements are greatly reduced. Electron impact ionization is utilized and the quadrupole analyzer has a resolution of approximately 1 amu. In

operation, the mass spectrometer can be programmed to periodically sweep through the entire spectrum or through any six mass numbers.

In mass spectrometry, molecules of a compound or the fragments of molecules are identified by the mass to charge ratio of their ions, and individual peaks can be monitored to detect and specify a particular compound. However, in the real world, an enormous number of materials are present even in the cleanest environment, and many of these can permeate through the membrane separator. At every mass number in the useful range of the instrument, there is at least a detectable level, and often a relatively high level of ions resulting from the background constituents. Thus, the detection threshold and specificity of the mass spectrometer are very much dependent on the compound to be detected and the environment in which the instrument is used. For instance, the major mass peaks of acetic anhydride coincide with regions of very high background. One obtains better sensitivity by relying on a minor peak of acetic anhydride at 60 amu for detection even though it is only 2% of the strength of the major peak at 43 amu.

The sensitivity of the mass spectrometer was determined with nitrogen or air as the carrier gas in the dilution system. The temperature setting on the probe and membrane separator depended on the material to be detected and ranged from ambient for perchlorethylene to 130°C for TNT. The system's threshold concentration level for perchlorethylene was approximately 0.1 PPB. Since this substance has major peaks in a very low background region of the spectrum, and since it is very efficiently transmitted by the separator, the value of 0.1 PPB should come close to representing the ultimate sensitivity of the instrument for a material in the cleanest environment. The threshold levels for other compounds of interest were 4 PPB for acetic anhydride, 25 PPB for TNT, and 75 PPB for heated cocaine. All of the above values were found in a computer-assisted mode.

The mass spectrometer is the most specific of all the systems evaluated. One can virtually eliminate false detections by using many mass numbers to identify or confirm the presence of vapors of a particular compound. However, the price to be paid for such certainty is a reduction in the detection threshold to that for the weakest of the chosen mass peaks. Interferences also can reduce the operational capabilities by producing a high background level at the major peaks of a compound, thereby requiring either larger increments in signal for a detection, or choice of a set of weaker mass peaks. Interferences are additive in the sense that many compounds can contribute to background at each mass number. As a result it is very difficult to predict the detection threshold of the mass spectrometer

in a given environment without a detailed knowledge of that environment.

D. MODEL 27 GELIGNITE DETECTOR AND MODEL 58 EXPLOSIVE DETECTOR

The Model 27 and Model 58 Detectors are portable detection systems consisting of three basic components: (1) a handheld sensing unit, (2) an electronic control box, and (3) a cylinder of high purity argon. The Model 27 detector is shown in Figure 4. In operation, ambient air is drawn into the inlet of the sensing unit and impinges upon a silicone membrane similar to those used in the separator of the mass spectrometer. The internal configuration of this portion of the units is diagrammed in Figure 5. The vapors which are transmitted through the membrane are then swept from its inner surface into the electron capture detector by a continuous argon flow. Vapors of compounds with an electron affinity, such as most explosives, reduce the standing current of the electron capture detector and are detected. One hopes to be able to distinguish explosives from other materials by the unit's recovery time following a detection.

While the Model 27 and Model 58 detectors operate on the same principle, the latter has several additional features. The most important of these is a variable temperature oven which surrounds part of the inlet, the membrane, and the electron capture detector. The oven can be set to maintain temperatures from 50°C to 150°C, in steps of 25°C, for the purposes of reducing adsorption on the detector's inner surfaces and of enhancing transmittance of vapors through the membrane. The other feature is an "automatic zero" control which suppresses slow signals associated with detector drift. The power requirements of the oven are met by an external battery pack.

Sensitivity measurements were performed on both of the models. The Model 27 detector showed a threshold concentration of approximately 0.2 PPB for EGDN although it was insensitive to TNT. The Model 58 Explosive Detector had a threshold concentration of slightly less than 0.1 PPB for EGDN with the oven set at 75°C. For TNT its threshold concentration was 0.2 PPB, with an oven temperature of 150°C. These instruments were by far the most sensitive detectors of explosives.

There are specificity problems with these detectors, particularly when the Model 58 is operated at temperatures above 100°C. Halogenated compounds, such as freon and perchlorethylene, have sensitivities comparable to that for EGDN. Other common

compounds such as gasoline give false detections. Fortunately, at near-ambient temperatures the recovery time following a detection is much longer for explosive vapors than other vapors. An experienced operator can recognize characteristic recovery times for explosive vapors. However, at the elevated temperatures required for detection of many explosives such as TNT, the recovery time is quite short for all compounds. Above 100°C there is little possibility of distinguishing detections of explosives and non-explosives. Nonetheless, since the Model 58 detector not only is much more sensitive to, but also is the only operationally effective detector for TNT and other low vapor pressure explosives, this lack of specificity must be accepted for the present. At this time a Model 62 explosive detector is being introduced which basically incorporates a chromatographic column into the Model 58 detector in an effort to solve the specificity problem. This detector has not been evaluated.

E. EXPLOSIVE DETECTION DOGS

One of the more unique methods of vapor detection is the use of detector dogs. Although the ability of dogs to be trained to detect and follow various odors is universally accepted, very little effort has been expended to determine concentration thresholds for compounds of interest. Three dogs trained by personnel at Southwest Research Institute were used in an attempt to determine approximate sensitivity level for an explosive vapor.

The detector dogs were trained and sensitized on a single vapor, and since they had shown a capability for detecting dynamite under a previous USAIWL program, EGDN was selected as the material for evaluation. This also allowed a direct comparison to be made between the trained dogs and the Model 27 Gelignite Detector. A special dilution system and three-funnel sampling chamber were constructed for the tests. There were two basic combinations of funnels for each test trial: (1) one of the three funnels had an EGDN sample, positive sample, and (2) none of the three funnels had an EGDN sample in it, negative sample. Positive and negative samples, as well as the location of the EGDN sample, were randomized.

The analysis of the tests verified the high accuracy of the dog in detecting vapors above a vial of undiluted EGDN (100% correct tests on positive samples, 95% correct tests on negative samples). At 100 PPB, the accuracy on positive samples had dropped to 56% and negative samples were indicated correctly during 58% of those tests. For tests conducted at 40 PPB, accuracy for both positive and negative samples had dropped to 33 1/3%. Since sample size was very small, statistically strong statements cannot be made concerning these tests.

III. CONCLUSIONS

The results of the detector evaluations are tabulated below:

Detection System	Specificity	Sensitivity
IMS	Very poor	A.A.* - 4 PPB EGDN - 25 PPB
Bioluminescent Sensor System	Fair	A.A.* - 24 PPB EGDN - 15 PPB TNT - 30 PPB
Mass Spectrometer	Excellent	A.A.* - 4 PPB TNT - 25 PPB Cocaine - 75 PPB
Model 27, Gelignite Detector	Good	EGDN - 0.2 PPB
Model 58, Explosive Detector	Fair to Good	EGDN - 0.1 PPB TNT - 0.2 PPB
Trained Dogs	Undetermined	EGDN - >100 PPB

* Acetic Anhydride

For detection of explosives, the Model 58 Explosive Detector is clearly the most sensitive as well as versatile detector, in that it responds to many explosive compounds. It is the operationally superior detection system for most situations. For detection of narcotics or location of covert narcotic production facilities, the Quadrupole Mass Spectrometer and the Bioluminescent Sensor System are recommended. Aside from considerations of cost and portability, the choice of a detector should be governed by operational environment and the degree of certitude required.

IV. REFERENCES

A. Wall, William A.; Gage, Herbert M. and Swisher, Joe A., Preliminary Evaluation of Vapor Detection Systems, Part I Gelignite Detector (U), Technical Note No. 73-04, US Army Land Warfare Laboratory, March 1973, AD 911589L.

B. Reports on the evaluations of the IMS, Dual Channel Bioluminescent Sensor, Model 58 Explosive Detector, Mass Spectrometer and Detector Dogs are pending.

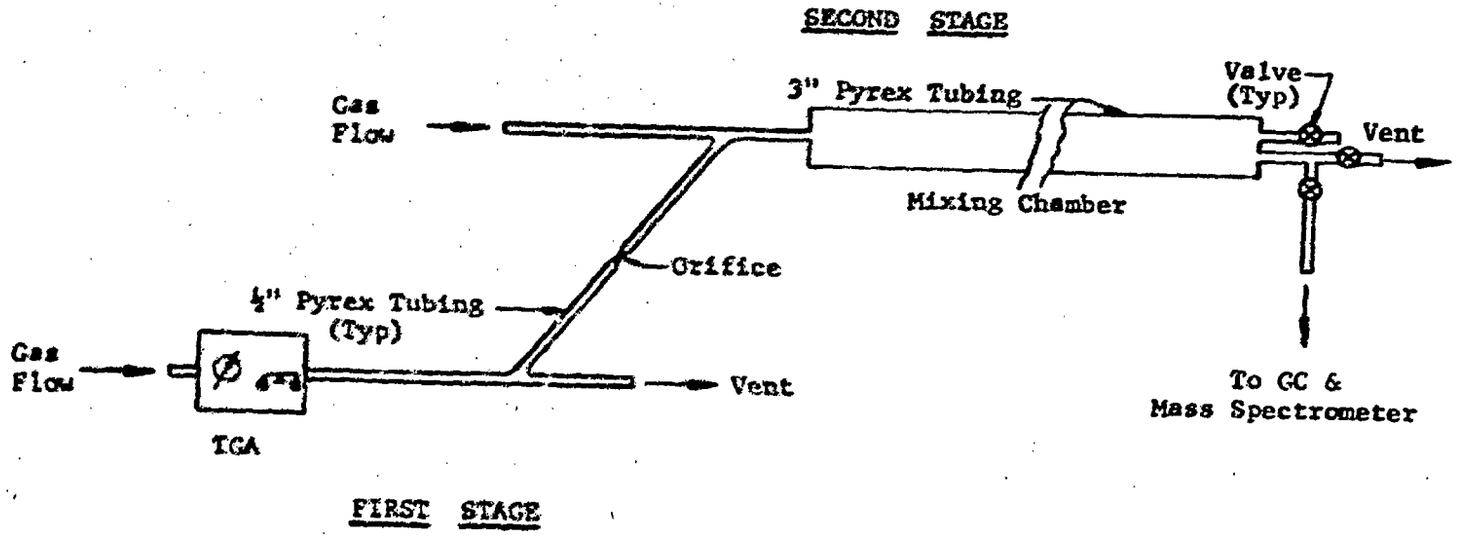
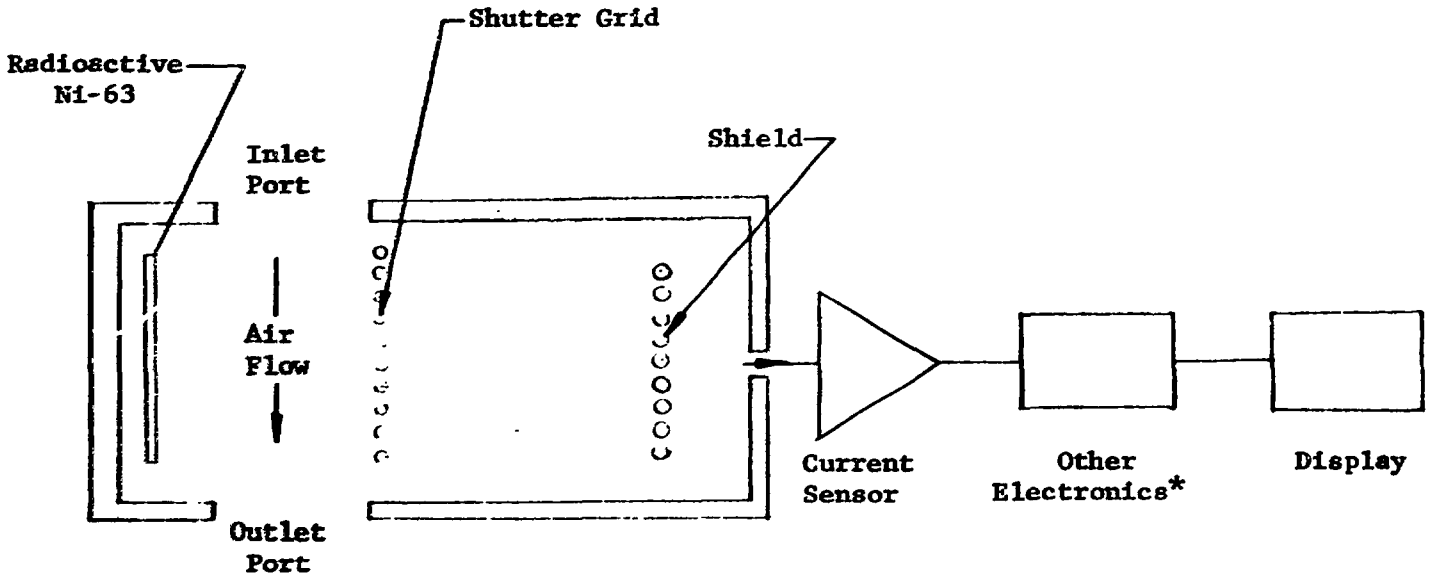


Figure 1. Two-Stage Dilution System



* Low-pass and high-pass filters
and gain control

Figure 2. Ion Mobility Spectrometer Schematic

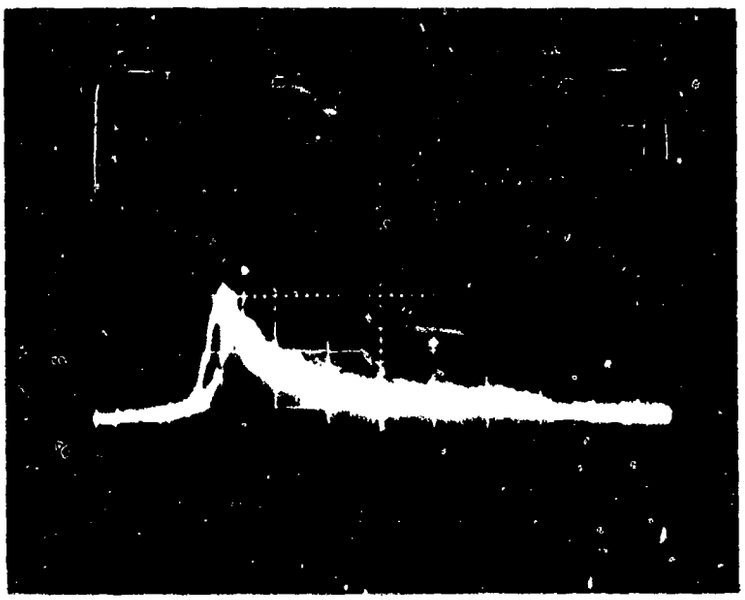


Figure 3(a). Spectra* of Ion Mobility Spectrometer for Acetic Anhydride at 5 PPB

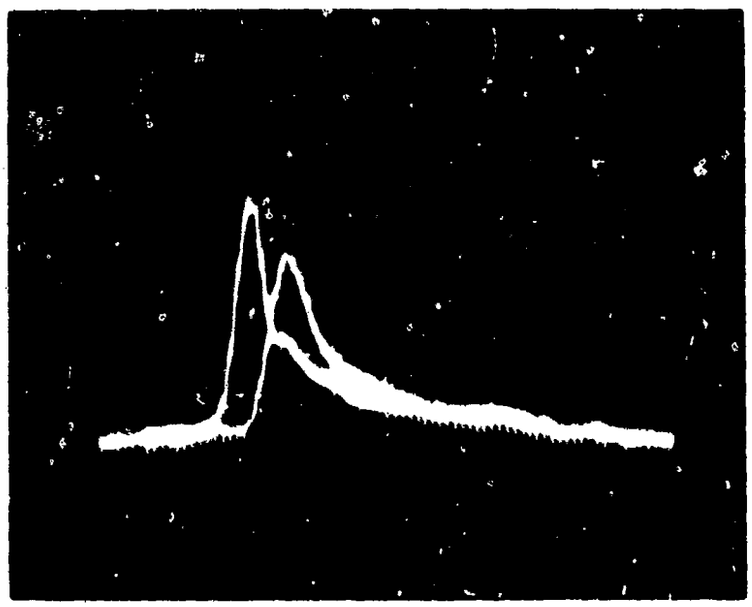


Figure 3(b). Spectra* of Ion Mobility Spectrometer for Acetic Anhydride at 15 PPB

* Clean air spectrum to the left is stored and used as a reference.

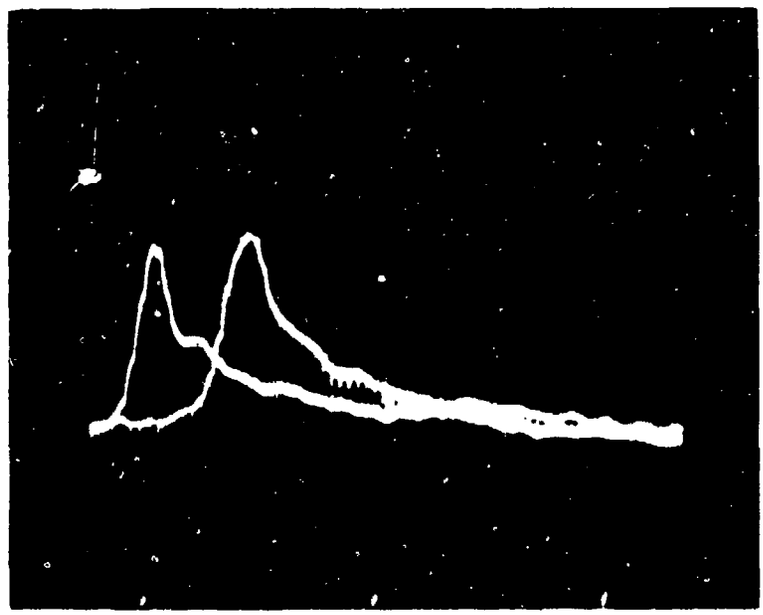


Figure 3(c). Spectra* of Ion Mobility Spectrometer for Acetic Anhydride at 36 PPB

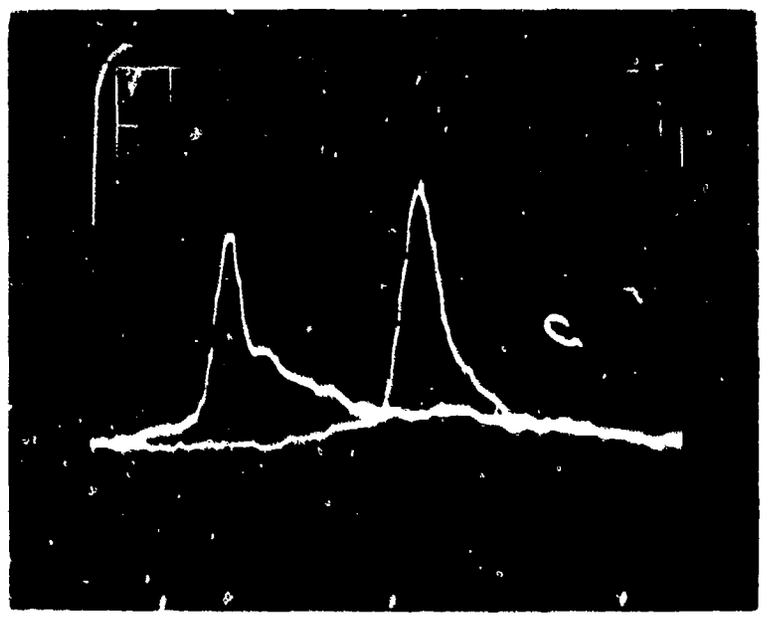


Figure 3(d). Spectra* of Ion Mobility Spectrometer for Acetic Anhydride at 257 PPB

* Clean air spectrum to the left is stored and used as a reference.

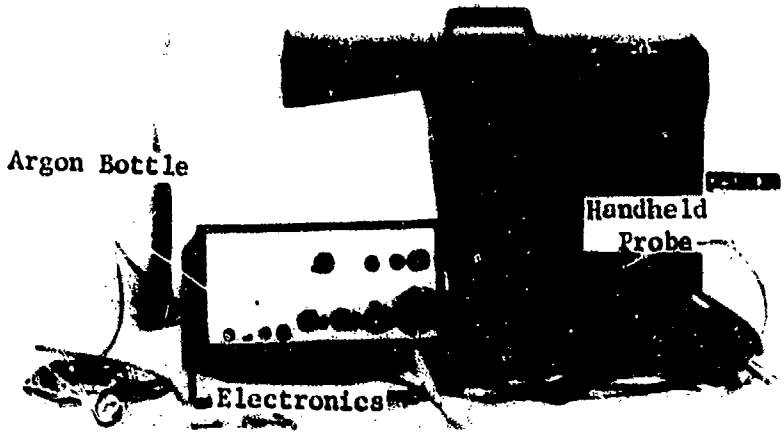


Figure 4. British Gelignite Detector, Model 27

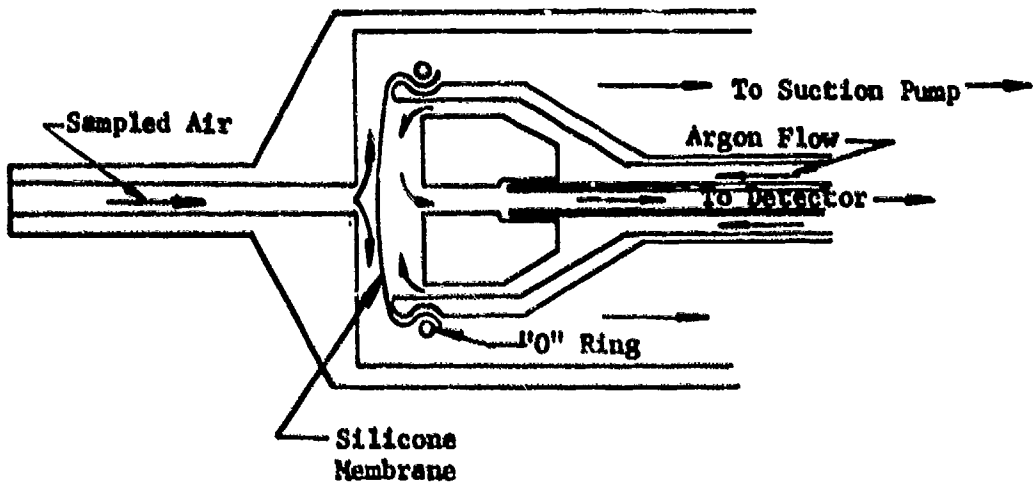


Figure 5. British Gelignite Detector Probe, Model 27